STUDIES IN THE ANALYTICAL CHEMISTRY OF SODIUM

I. FLUOALUMINIC ACID AND FLUOFERRIC ACID AS REAGENTS FOR SODIUM

by

E. BATES AND R. BELCHER

Department of Chemistry, The University, Aberdeen (Scotland)

The reagents normally used for the detection and determination of sodium are potassium dihydrogen antimonate, potassium dihydroxytartrate, caesium bismuth nitrite and the double uranyl acetate reagents containing zinc, magnesium, nickel, copper, manganese, or cobalt. By far the most effective of these reagents are the double uranyl acetate reagents. Caesium bismuth nitrite and potassium dihydroxytartrate are unstable and less sensitive, and the former reagent is too expensive for more than occasional use. Potassium dihydrogen antimonate is the least sensitive, although it is the usual standby in qualitative analysis.

Some other reagents have been recommended, but critical studies of their properties have yet to be made. Since it is desirable that their properties should be investigated further and, if possible, extended to quantitative work, particularly since uranium salts are now unobtainable, an examination has been made of the reactions of these less common reagents for sodium.

Fluoaluminic acid was recommended as a reagent for sodium by WILKES[1] in 1909. He prepared the reagent by treating aluminium hydroxide with hydrofluoric acid in a platinum dish for two days. An equal volume of saturated copper or nickel acetate was added to reduce the hydrogen ion concentration, since neither of these cations yielded precipitates with the reagent. After boiling and filtering the mixture, an equal volume of 50% ethanol was added. WILKES claimed that his reagent would detect 1 part of sodium in 20000. Potassium and ammonium did not yield precipitates, but lead, silver, and the alkaline earths formed insoluble compounds.

WILKES also studied the effect of substituting related elements for the aluminium. By replacing the aluminium hydroxide by ferric hydroxide, a reagent was obtained which gave a light brown precipitate with sodium. Beryllium and chromic hydroxide did not form reagents which precipitated sodium. It is stated in the paper that the quantitative applications of the reagent were to be examined,

References p. 408.

but we were not able to trace any record of such experiments, nor could we find any reference to later work in which this reagent was used.

Our own findings show that whilst the reagent will differentiate between sodium and potassium within certain limits, the reaction is not very sensitive.

When fluoaluminic acid was added to solutions containing 4 mg of sodium per ml or more, positive results were obtained. Below this concentration it was impossible to detect sodium. Potassium dihydrogen antimonate will detect sodium down to a concentration of 1 mg per ml[2]; in ethanolic solution it will detect 0.25 mg per ml.

Fluoaluminic acid does not give an immediate positive reaction with potassium at a concentration of 20 mg per ml, but a small precipitate appears after leaving the solution overnight.

Because of the poor sensitivity the quantitative applications of the reagent were not investigated.

Fluoferric acid proved to be even less sensitive. At a concentration of 10 mg per ml of sodium the test failed.

EXPERIMENTAL

Aluminium hydroxide, which had been air-dried, was added to hydrofluoric acid in a platinum dish. More aluminium hydroxide was added when the previous amount had dissolved completely in the acid. The mixture was allowed to stand for one week. Further addition of aluminium hydroxide were made during this time until no more dissolved. An equal volume of a solution of saturated copper acetate was added and the mixture boiled and filtered. An equal volume of 50% ethanol was added to the filtrate.

Some esterification occurred, for after standing for a short period the reagent smelt strongly of ethyl acetate. This did not appear to vitiate the properties of the reagent for the same results were obtained with fresh reagent and samples which had been prepared for several days.

Fluoferric acid was prepared similarly but ferric hydroxide was substituted for the aluminium hydroxide.

The tests were made by adding varying amounts of reagent (usually an equal volume) to 1.5 ml of a solution of sodium or potassium chloride. It was found that either the test solution or the reagents had to be hot otherwise the precipitate was gelatinous.

Six different preparations of each reagent were made. The test at each concentration was done between 10 and 20 times. The same results were obtained in every case.

The results of these tests are included in the following tables.

References p. 408.

TABLE I

THE REACTION OF FLUOALUMINIC ACID WITH SODIUM AND POTASSIUM CHLORIDES

Test Solution ml	Na present mg	K present mg	Reagent ml	Result
1.5	30.0	—	1.5	Immediate precipitate
1.5	15.0	—	1.5	Id.
1.5	7.5	—	1.5	Turbidity after 5 min increasing to small precipitate on standing
1.5	6.0	—	1.5	Id.
1.5	6.0	—	4.5	Id.
1.5	3.0	—	1.5	No precipitate even after standing overnight
1.5	3.0	—	3.0	Id.
1.5	3.0	—	6.0	Id.
1.5	—	30.0	1.5	Very small precipitate after standing overnight
1.5	—	15.0	1.5	No precipitate after standing overnight

TABLE II

THE REACTION OF FLUOFERRIC ACID WITH SODIUM AND POTASSIUM CHLORIDES

Test Solution ml	Na present mg	K present mg	Reagent ml	Result
1.5	30.0	—	1.5	Faint light brown precipitate after shaking for 5 min. Increased on standing
1.5	15.0	—	1.5	No precipitate even after standing overnight
1.5	15.0	—	4.5	Id.
1.5	—	30.0	1.5	Id.

This communication consists of a portion of a thesis submitted by ERIC BATES in partial fulfilment of the requirements for the Degree of Master of Science, London University.

SUMMARY

Fluoaluminic acid and fluoferric acid have been examined as reagents for the detection of sodium. Fluoaluminic acid fails to give a positive reaction at a concentration of less than 4 mg of sodium per ml. Fluoferric acid fails to give a positive reaction at a concentration of 10 mg of sodium per ml. Although the reagents will differentiate between sodium and potassium at favourable concentrations neither is sufficiently sensitive to recommend as a test for sodium.

References p. 408.

RÉSUMÉ

L'acide fluoalumique et l'acide fluoferrique ont été étudiés en vue de leur utilisation comme réactifs inférieure à sodium. L'acide fluoaluminique ne donne plus de réaction avec le sodium à une concentration inférieure à 4 mg par ml, et l'acide fluoferrique, à une concentration de 10 mg de sodium par ml. Bien que ces 2 réactifs permettent de différencier le sodium du potassium, leur sensibilité n'est pas suffisante pour pouvoir les recommander.

ZUSAMMENFASSUNG

Fluoraluminiumsäure und Fluoreisensäure wurden als Reagens für den Nachweis von Natrium geprüft. Fluoraluminiumsäure gibt keine positive Reaktion wenn die Natriumkonzentration geringer ist als 4 mg pro ml; für Fluoreisensäure liegt diese Grenzkonzentration bei 10 mg pro ml. Obwohl diese beiden Reagentien zwischen Natrium und Kalium zu unterscheiden erlauben, so sind sie doch nicht genügend empfindlich, um als Probe auf Natrium empfohlen werden zu können.

REFERENCES

1 W. A. R. WILKES, *Proc. Cambridge Phil. Soc.*, 15 (1909) 17.
2 I. M. KOLTHOFF, *Pharm. Weekblad*, 60 (1923) 1251.

Received January 5th, 1949